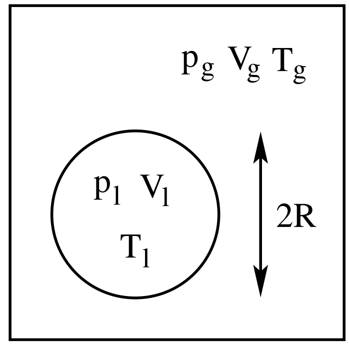
Condensation and evaporation [tln32]

Supersaturated gases and *superheated* liquids owe their metastable existence to the surface tension σ. Consider a liquid droplet in equilibrium with the surrounding vapor, implying $T_l = T_g,\ \mu_l = \mu_g$, and $p_l > p_g$ because of surface tension.

For a vapor bubble surrounded by liquid, the argument proceeds along analogous lines.



Work done if droplet expands or contracts: $\delta W = -p_l dV_l - p_g dV_g + \sigma dA$.

Grand potential: $\Omega(T,V,\mu) = -p_l V_l - p_g V_g + \sigma A$.

$$\Rightarrow\ \Omega(T,V,\mu) = -\frac{4\pi}{3}R^3 p_l - \left(V_{tot} - \frac{4\pi}{3}R^3\right)p_g + 4\pi R^2\sigma.$$

Mechanical equilibrium: $(\partial\Omega/\partial R)_{T,V,\mu} = 0\ \Rightarrow\ 4\pi R^2(p_g - p_l) + 8\pi R\sigma = 0.$

Excess pressure in droplet: $p_l - p_g = 2\sigma/R$.

Gibbs-Duhem equations (with $dT = 0$), $N_l d\mu_l = V_l dp_l, N_g d\mu_g = V_g dp_g$.

Chemical equilibrium: $d\mu_l = d\mu_g\ \Rightarrow\ (V_l/N_l)dp_l = (V_g/N_g)dp_g$.

Differential excess pressure: $d(p_l - p_g) = \dfrac{V_g/N_g - V_l/N_l}{V_l/N_l}dp_g = d\left(\dfrac{2\sigma}{R}\right)$.

Use $\dfrac{V_g}{N_g} \gg \dfrac{N_l}{V_l},\ \dfrac{V_g}{N_g} \simeq \dfrac{k_BT}{p_g}\ \Rightarrow\ \dfrac{k_BT/p_g}{V_l/N_l}dp_g = d\left(\dfrac{2\sigma}{R}\right)$.

Integrate $\dfrac{dp_g}{p_g} = \dfrac{V_l}{N_l k_B T}d\left(\dfrac{2\sigma}{R}\right)$ from ∞ to R.

$$\Rightarrow\ \ln\frac{p_g(R)}{p_g(\infty)} = \frac{2\sigma V_l}{RN_l k_B T} = \frac{2\sigma m}{R\rho_l k_B T}\ \Rightarrow\ p_g(R) = p_g(\infty)\exp\left(\frac{2\sigma m}{R\rho_l k_B T}\right).$$

Only liquid droplets of a particular radius R_c coexist with the supersaturated gas phase. Droplets with $R < R_c$ will shrink. Droplets with $R > R_c$ will grow. Hence the condensation process at pressure $p = p_g(R_c)$ can be initiated by the presence of droplets with radius $R > R_c$.

Metastability depends on the absence of droplets with radius $R > R_c$. The boundary of the metastable region (spinodal line) corresponds to a value of R_c comparable to the molecular radius. Supersaturation cannot be pushed beyond that point.